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MAJOLICA PRODUCTS BASED ON RAW MATERIAL FROM TUVA

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The possibility of producing majolica based on local materials from Tuva is demonstrated. The thermal treatment of products is performed under a decreased pressure, which significantly intensifies sintering and improves properties of finished materials.

The only ceramic product produced in the Republic of Tuva is solid brick. Therefore, the development of new products is a topical problem that calls for studying local mineral resources and developing new technologies.

It is known that the specifics of majolica technology (slip casting, glazing) and the properties of finished materials (water permeability, heat resistance) are related to certain requirements imposed on mineral materials. According to the data in [1], materials for majolica products have particular flow properties and specific ratios between high-melting ($Al_2O_3 : SiO_2$) and alkali and alkali-earth oxides ($R_2O : RO$).

It was earlier established [2] that local argillaceous rocks in Tuva are low-melting with prevalence of montmorillonite and hydromica. They have significant fluctuations in the granular composition fractions, a high content of ferrous compounds and carbonates, and a narrow sintering interval. Having analyzed the chemicomineralogical specifics and economical parameters of argillaceous deposits (volume of reserves, bedding conditions, and proximity to the transport network), we have selected clay from the Krasno-yarskoe deposit. Preliminary studies of clays from different deposits indicated that the slip from pure Krasno-yarskoe clay has the best liquescence and fluidity, the minimal thickening capacity, and molded preforms are less prone to deformation and crack formation. The chemical composition of Krasno-yarskoe clay is as follows (here and elsewhere, wt.%): 56.63 SiO_2, 15.13 Al_2O_3, 0.97 TiO_2, 6.30 Fe_2O_3, 5.78 CaO, 2.85 MgO, 1.08 K_2O, 1.25 Na_2O, 0.87 SO_3, and 8.35 calcination loss. The clay has a high content of iron oxides and alkali-earth elements. The refractoriness temperature is 1220°C.

X-ray phase analysis indicated that the main mineral in Krasno-yarskoe clay is montmorillonite. Hydromica is present in insignificant quantities. Impurities are represented by quartz, orthoclase, calcite, and goethite. The share of argillaceous, dust-like, and sandy particles in the granulometric composition is 28 – 35, 38 – 52, and 18 – 26%, respectively. Based on the content of particles below 1 μm, Krasno-yarskoe clay belongs to the low-dispersion group, since the content of the specified particles is 19 – 22%. The plasticity number of this clay is 14.

The following method was used in our study. Material samples dried to a constant weight were proportioned and loaded together into a ball mill. Water was added to reach a required slip moisture. The milling of materials continued to a residue not more than 2% on a No. 0063 sieve. After casting slip into gypsum molds and drying it to a constant weight at 100 – 105°C the products were subjected to a first and a second firing in the laboratory vacuum electric furnace.

The mixture composition was selected based on the flow and technological properties of slip (fluidity, sample setting rate, degree of filling molds) and taking into account the service characteristics of finished products (water absorption, water permeability, heat resistance etc.). The grog additive used to control the slip characteristics was crock based on the same Krasno-yarskoe clay. Cullet was introduced to improve sinterability. The thinning additive controlling the rheological properties of slip and ensuring the steadiness of the suspension was soda ash in the amount of 0.2% (above 100%) whose effect in based on the ion-exchange processes on the surface of the solid slip particles. The compositions of experimental mixtures are listed in Table 1. The obtained slips had the following parameters: moisture 52 – 54%, fluidity 10 – 12 sec (for the diameter of the opening equal to 6 mm), milling fineness 0.8 – 1.0% (residue on No. 0063 sieve), and thickening coefficient 2.0 – 2.2.

The traditional flux (cullet) was introduced to improve the sintering of mixtures. It should be noted that samples of pure Krasno-yarskoe clay fired at the temperatures of 900 and 1000°C had water absorption of 18.8 and 14.1%, respectively, which indicates a high porosity of fired products.

In order to significantly intensify the sintering of ceramic mixtures, the first firing of samples was carried out under a decreased pressure equal to 133 – 399 Pa. For this purpose a

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TABLE 1

Mixture	Weight content, %		
	Krasno-yarskoe clay	crock	cullet
1	90	10	–
2	80	20	–
3	80	15	5
4	80	10	10
5	75	10	15

TABLE 2

Mixture	Water absorption, %, at firing temperature, °C		
	900	950	1000
1	17.4	15.6	14.7
2	18.6	16.7	15.9
3	16.2	14.4	13.3
4	14.1	13.2	12.3
5	12.5	11.2	10.4

vacuum electric furnace was constructed. The advantage of firing ceramics under a decreased pressure is discussed in [3] stating that sintering in this case starts at a temperature of 100°C lower than under normal pressure.

The effect of additives on sintering of products that are preliminarily fired under decreased pressure is shown in Table 2. The main criterion in selecting the optimum mixture was the water absorption of samples. Mixtures 1 and 2 containing crock had higher porosity and, accordingly, a high water absorption (14.7 – 18.6%). At the same time, the introduction of crock prevents drying defects (deformations, cracks). The content of the crock in a mixture is limited to 10%, since a further increase in this additive to 20% causes excessive water absorption in the product (over 16%). The best composition among the ones containing cullet is mixture 4 with 10% cullet, whose water absorption is within the interval of 13.2 – 14.1% at the firing temperatures of 950 and 900°C. The fact is that, owing to the chemicomineralogical specifics of Krasno-yarskoe clay, prefired articles with water absorption below 13% poorly absorb glaze. Products made of mixture 3 have water absorption of 14.4 – 16.2% at the firing temperatures of 900 – 950°C, however, their water impermeability is inferior to that of the products made from mixture 4. Apparently, 5% cullet additive has an insufficient effect on the sintering of ceramic mixture 3.

Therefore, for further experiments we chose mixture 4 fired at 900°C under a decrease pressure with an isothermal exposure for 1 h. The intense sintering of a mixture containing 10% cullet and the formation of an optimal porous structure (water absorption 13 – 14%) is primarily due to the chemicomineralogical specifics of this material. It is noted in [4] that sintering of majolica mixtures based on low-melting clays is the fastest when the sum of alkali and alkali-earth oxides ($RO + R_2O$) is within the limits of 10 – 12%. If the $RO : R_2O$ ratio is equal to 1.0 – 2.5, the sintering is further intensified. In our case (taking into account 10% cullet) this ratio reaches its optimum values. In general the additional introduction of fluxes leads to the formation of a great amount of the vitreous phase, which facilitates the formation of a structure with required water absorption.

The frit glaze produced at the Universal Company (city of Novokuznetsk) was used for glazing experimental samples. Its characteristics are as follows: moisture 45%, density 1.34 g/cm^3, milling fineness — residue on a No. 0063 sieve not more than 0.5%, fluidity 8 sec. The products were glazed by immersion and by spraying. The second firing was carried out in the electric furnace at 960°C with an isothermal exposure of 0.5 h. The glaze on finished products was well fused, lustrous, and without pinholes.

Finished products (vases, mugs, salad bowls, wine cups, etc.) were tested according to standard OST 21-52–82. Their water absorption was 11 – 12%, they were water-impermeable and withstood over 8 thermal cycles. The CLTE of the proposed mixture in the temperature interval of 20 – 600°C was equal to 6.8×10^{-6} K^{-1}.

Thus, a local poorly sintering clay with additives has been used to develop a ceramic mixture for majolica products, in which the $RO : R_2O$ ratio is within the limits of 0.25 – 0.30. To intensify sintering, preliminary heat treatment was performed under a decreased pressure, which makes it possible to decrease the product porosity, lower the firing temperature, and shorten the cycle duration.

The obtained results have been used to develop a technological schedule for the production of majolica articles at the Narodnye Promysly Company (city of Kyzyl).

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